# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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| In re Application of: | : | Mark Philip D'Evelyn et al. |
| Application No. | : | 09/683,658 |
| Filed | : | January 31, 2002 |
| Examiner | : | Jennifer A. Leung |
| Group Art Unit | : | 1764 |
| Confirmation No. | : | 1463 |
| Title | : | PRESSURE VESSEL |

## APPEAL BRIEF

(In compliance with 37 CFR § 41.37)

Mail Stop: Appeal Brief – Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

In response to the Office Communication dated July 18, 2006, Appellant submits this Appeal Brief and the fee specified in 37 CFR § 41.20(b)(2) ($500.00 for a large entity).

## Real Party in Interest – 37 C.F.R. 41.37(c)(1)(i)

The General Electric Company is the real party in interest.

## Related Appeals and Interferences – 37 C.F.R. 41.37(c)(1)(ii)

None aware of.

## Status of Claims – 37 C.F.R. 41.37(c)(1)(iii)

On July 18, 2006 Appellant appealed from the final rejection of claims 104-106, 112, 130, 145-155. No claims stand withdrawn. No claims are allowed or objected to. Claim 1-103, 107-111, 113-129, 131-144 are cancelled. Claims 104-106, 112, 130, 145-155 are currently pending and the subject of this Appeal.

## Status of Amendments – 37 C.F.R. 41.37(c)(1)(iv)

All amendments have been entered. Accordingly, claims 104-106, 112, 130, 145-155 are pending and the subject of Appeal, and there are no outstanding amendments.

## Summary of Claimed Subject Matter – 37 C.F.R. 41.37(c)(1)(v)

The only pending independent claims are claims 104 and 146.

Independent claim 104 discloses an apparatus that includes a capsule 12 (see paras. [0025]-[0026]), a restraint 24 (see para. [0024]), and an energy source 18 (see para. [0021]). The capsule 12 has an interior surface 52 defining a volume 54, and the capsule 12 can receive a material and a fluid in the capsule volume 54. It is noted that at this point in the claim, the inference to the material and to the fluid does not make them elements or limitations of the claim, however they are mentioned to provide a standard against which the functionality of the capsule 12 may be measured. The fluid becomes

supercritical at least at a determined temperature and a determined pressure (see para. [0045]). The capsule 12 both is sealable, and maintains a seal to the material and to the fluid while the capsule 12 is subject to the determined temperature and to the determined pressure.

The restraint 24 has an interior surface defining a chamber, and the chamber is configured to receive the capsule 12, and the restraint 24 resists a pressure exerted by the capsule against the restraint interior surface and to maintain the chamber at a substantially constant volume.

The energy source 18 supplies sufficient thermal energy to the capsule 12 so that the determined temperature is at least about 800 degrees Celsius. The fluid is responsive to the thermal energy both to become supercritical at the determined temperature and at the substantially constant volume in the chamber, and to increase the pressure in the volume 54 to at least the determined pressure. Again, it is noted that the fluid provides the frame of reference against which the positively claimed elements are measured.

With regard to claim 146, an apparatus 100 is provided that includes a capsule 12, a restraint 24, and an energy source 18. The capsule 12 has an interior surface 52 defining a volume 54, and the capsule 12 has disposed within the volume an amount of metal material and an amount of ammonia (see para. [0045]). This differs from claim 104 in that the contents of the capsule 12 are positively recited, and are claim elements. The capsule 12 both is sealable to maintain an internal pressure, and is functionally capable of maintaining a seal to the amount of ammonia while the capsule is subject to a determined temperature and to a pressure in a range of from about 5 kBar to about 80 kBar.

The restraint 24 has an interior surface defining a chamber that can receive the capsule 12. The restraint 24 resists a pressure exerted by the capsule 12 against the restraint interior surface and to maintain the chamber at about a constant volume (see para. [0031]). The restraint 24 does not provide an active pressure load radially inward toward the capsule 24 (see para. [0031]).

The energy source 18 supplies thermal energy to the capsule 12 such that the ammonia responds to the thermal energy at the constant volume in the chamber to

increase the pressure in the chamber and to become supercritical ammonia (see para. [0031]). The supercritical ammonia reacts with the metal material to form a metal nitride composition (see para. [0039]).

Appellant notes that there is no "means for" or "step plus function" language under 35 U.S.C. §112, paragraph six in the independent claim.

## Grounds of Rejection to be Reviewed on Appeal – 37 C.F.R. 41.37(c)(1)(vi)

1. Whether claims 150-152 were properly rejected under 35 USC § 112 as being indefinite.

2. Whether claims 104-106, 112, 130 and 145 and 154 were properly rejected under 35 USC § 102 as being anticipated by Wilson et al. (US 3,473,935).

3. Whether claim 106 was properly rejected under 35 USC § 103 as being unpatentable over Wilson et al. in view of Hall et al. (US 2,974,610).

4. Whether claims 146-153 were properly rejected under 35 USC § 103 as being unpatentable over Wilson et al. in view of Flanigen (US 3,567,643).

## Argument – 37 C.F.R. 41.37(c)(1)(vii)

The Examiner has erred in fact, and an error in fact is an error in law. As discussed in detail below, the Examiner has improperly rejected the pending claims as indefinite, or as obvious over the cited references. Accordingly, the Appellant respectfully requests withdrawal of these rejections of the claims. The rejections are discussed in the order addressed by the Examiner in the previous Office Action.

### 1. Claims 150-152 are not indefinite under 35 USC § 112.

Claims 150 - 152 were rejected as being indefinite under 35 USC § 112. It was unclear to the Examiner "as to the structural limitation ...because the 'metal nitride composition', the 'single crystal metal nitride composition' and the aluminum nitride' are products formed by the apparatus, and are therefore not considered to be part of the apparatus". Appellant responds that in the same way that a bread mixer differs from a

cement mixer based on a reference to the material produced, so to does one apparatus capable of processing one type of material differ from another apparatus capable of processing another type of material – based at least in part on a reference to the material produced thereby. Appellant grants more detail may be needed, but the reference to the material itself is neither indefinite nor is it unclear. If the parent claim is patentable, than the further characterization, however slight, that excludes some apparatuses and includes others within the scope of the parent claim should be sufficient to overcome a rejection under 35 USC § 112.

  2. Claims 104-106, 112, 130 and 145 and 154 are not anticipated by Wilson et al. (US 3,473,935).

  With regard to the rejection under 35 USC § 102(b) as being anticipated by Wilson et al., Appellant submits that the apparatus shown or disclosed differs from the invention as defined at least in independent claims 104 and 146. Ignored are the functional recitations of "to maintain the chamber at a substantially constant volume" and "to maintain the chamber at about a constant volume".

  The core 16 indicated in the Office Action as anticipating the restraint is not bounded on at least two sides as shown in Fig. 1. The top and the bottom of the core 16 of Wilson et al are open. The core 16 of Wilson et al. provides, at best, two-dimensional control, and cannot provide three-dimensional control. "Volume" is a three-dimensional unit. A prior art element having both the function and structure of the restraint as defined in the independent claim is not shown. Accordingly, Appellant expects that a rejection based on an accumulation of prior art elements (the core 16 plus the two press pistons 23 and 24, or the core 16 plus the rings 11-15) would similarly not anticipate the independent claims. In summary, there is no corresponding structure in the cited art that has the structure and performs the function of at least one of the elements in each of the independent claims.

  While supercritical fluid may not be a positive element recitation in claim 104, the term does qualify as functional language modifying an attribute of a positively recited claim element. As functional language the term does have patentable weight if it sets definite boundaries on the patent protection sought. *In re Barr*, 444 F.2d 588, 170 USPQ

33 (CCPA 1971). Particularly, the term functionally qualifies a structural element that is positively set forth in clear language. A functional limitation defines something by what it can do, rather than by what it is (e.g., as evidenced by its specific structure). A functional limitation must be evaluated and considered, just like any other limitation of the claim, for what it fairly conveys to a person of ordinary skill in the pertinent art in the context in which it is used. A functional limitation may be used in association with an element to define a particular capability or purpose that is served by the recited element. An analogy may be had with reference to waterproof boots – the fact that there is no water currently in contact with those boots does not negate the substantive, functional qualifier of "waterproof".

The functional language used herein sets definite boundaries on the patent protection sought. *In re Barr*, 444 F.2d 588, 170 USPQ 33 (CCPA 1971). Further, the functional language precisely defines present structural attributes of the claimed element. *In re Venezia*, 530 F.2d 956, 189 USPQ 149 (CCPA 1976). By refusing to consider all of the terms and elements of the claims, Appellant submits that there is clear error in the rejections listed in the Office Action.

Claim 105 states "the restraint is operable to counterbalance pressure in the capsule". Wilson et al. discloses the core 16 is a tungsten carbide core (column 3, line 12). In lines 15-20 (still column 3), the bores, and counterbores cooperate with the pistons "...to impose pressure on the sample..." Appellant has gone to great lengths to indicate that actively imposing pressure differs from providing a counterbalancing pressure. The Office Action would vitiate that distinction.

Claims 112 and 130 depend from an allowable claim, and are therefore also allowable. Claim 130 defines functionally the quality, character or attribute of the restraint that is measurable as a pressure response. The "pressure response" is an inherent property of the restraint. For example, if an exemplary non-inventive capsule was placed in a moving press and did not self-pressurize - then for every percent increase in the dynamic press force there would be a corresponding non-linear increase in the capsule pressure. By contrast, if a self-pressurizing capsule were placed in a dynamic press then an increase in force from the dynamic press would increase the pressure both by direct

pressure from the press and from the pressure from the self-pressurizing capsule. By way of further contrast, if a self-pressuring capsule were placed in a static restraint subject to, for example, thermal expansion then the percent increase in pressure would differ relative to the other two postulated scenarios (all assume an increase in temperature or reference operation condition). In summation, the pressure response (or percentage ratios) differ based at least on the source of the pressure. As such, the claim limitation indicates where the pressure originates, and is a legitimate element of the claimed apparatus. It is not a variable of an intended process.

Claim 145 depends from an allowable claim and defines a capsule that can exert an internal a pressure of greater than about 60 kBar. Pressure limits for capsules or cells in Wilson et al. are disclosed to be up to 60 kBars (col. 2, line 58, and col. 3, line 44, respectively). For at least claim 145, Wilson et al. does not disclose or enable a pressure capability approaching the claim definition. Without disclosure or reasonable suggestion of the claim elements, there can be no anticipation.

3.   Claim 106 is patentable over Wilson et al. in view of Hall et al. (US 2,974,610).

Claim 106 was rejected under 35 USC § 103 over Wilson et al in view of Hall et al. Claim 106 recites a "heating system that includes the energy source and a temperature sensor, wherein the temperature sensor is disposed proximate to the capsule and is operable to sense a temperature of the capsule". The Office Action admits that Wilson et al. "is silent as to the control system being operable to provide a closed loop temperature control of the heating system, in response to a signal generated by a temperature sensor disposed proximate to the capsule". The Office Action continues, "it would have been obvious to one of ordinary skill in the art at the time the invention was made to provide a temperature sensor and to configure a closed loop temperature control scheme for the control system in the apparatus of Wilson et al. on the basis of suitability for intended use".

However, Appellant submits that this is not the standard for a *prima facie* case of obviousness. That a cited reference *may be* modified is not the standard, rather a reason for the combination or modification must be given. Clearly, Wilson et al did not believe

a sensor was necessary, otherwise they would have disclosed one. Similarly, Hall et al. does not disclose other elements of the claimed invention because that was not the intent or understanding of Hall et al. For the cited art to be combined, without the benefit of impermissible hindsight reconstruction, there must be some reason or motivation provided beyond mere "because it is well known in the art to connect a control system with a temperature sensor to enable precise, closed loop control of the reaction temperature". The closed loop control is disclosed in claim 106, and not disclosed in Wilson et al. Hall et al. provides no insight as to whether a control system as disclosed therein would be a boon to the invention of Wilson et al., or even if the combination would be basically functional to carry out the reaction of Wilson et al. who did not appear to need the modification the Office Action suggests.

In addition, the Office Action states that the replacement of manual means with automated means is obvious. That does not appear to be in dispute. Claim 106 includes a sensor, and Wilson et al. does not disclose such a structural or functional element. The Office Action attempts cure this deficiency by combining elements of Wilson et al. and Hall et al. The result of the combination is, unfortunately, a combination of a reaction that does not appear to need a sensor, and likely is workable in large temperature ranges, with a reaction that uses a sensor. Appellant submits that an explanation would be useful as to why one of ordinary skill in the art would take a simple and functional apparatus as shown in Wilson et al. and start adding components and control systems to increase the complexity and cost. As no such explanation has been proffered, Appellant submits that a *prima facie* case of obviousness has not been made, the rejection should be withdrawn, and a notice to that effect is respectfully requested.

4.  Claims 146-153 are patentable over Wilson et al. in view of Flanigen (US 3,567,643).

Claim 146 is rejected under 35 USC § 103 as being unpatentable over Wilson et al in view of Flanigen et al. Claim 146 defines a structure capable of maintaining a seal at a pressure range of from 5 kBar (about 75,000 psi) to about 80 kBar. Flanigen et al. shows an example of not more than 20,000 psi as indicated in the Office Action. It is not reasonable for one of one of ordinary skill in the art to expect that a seal designed for use

at a low pressure would be a suitable replacement for a situation that requires a minimum of about 3 times more pressure. It is not obvious what seal or seal mechanism would be sufficient for the different and extreme pressures, such as those defined in claim 146.

In summary of the arguments set forth, the Examiner errs both in fact and in law. The pending claims are not obvious in view of the cited art references (alone or in combination). The primary reference for all of the rejections does not show what it is purported to show, namely a substrate having the properties as defined in claim 1. The addition of any of the other cited reference similarly does not show the claimed substrate. Finally, the combination of any of the references does not disclose, teach or reasonably suggest the invention as defined in at least claim 1.

## Claims Appendix - – 37 C.F.R. 41.37(c)(1)(viii)

Appendix I containing a listing of the claims as pending in this Appeal is attached following the signature page of this Brief.

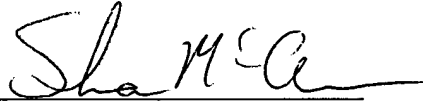## Evidence Appendix – 37 C.F.R. 41.37(c)(1)(ix)

An Appendix II containing a copy of the references cited in the arguments presented here is attached following the Claim Appendix of this Brief.

## Related Proceedings Appendix – 37 C.F.R. 41.37(c)(1)(x)

There are no related proceedings to this Appeal. An Appendix III stating that there are no related proceedings under 37 C.F.R. 41.37(c)(1)(x) is provided.

Appellant respectfully submits that the claims 104-106, 112, 130, and 145-155 define allowable subject matter over the cited art, and requests that the rejections to Claims 104-106, 112, 130, and 145-155 be withdrawn.

Respectfully submitted,

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_10/19/06_
Date

## Claims Appendix I under 37 C.F.R. 41.37(c)(1)(viii)

Following are a listing of claims as currently pending in the Application that is the subject of this Appeal.

Listing of Claims:

Claims 1-103 (cancelled)

Claim 104. (Previously presented)  An apparatus, comprising:

a capsule having an interior surface defining a volume, and the capsule is configured to receive a material and a fluid in the capsule volume, the capsule both is sealable, and is operable to maintain a seal while the capsule is subject to a determined temperature and to a determined pressure, and the fluid is operable to become supercritical at least at the determined temperature and the determined pressure;

a restraint having an interior surface defining a chamber, and the chamber is configured to receive the capsule, and the restraint is responsive to resist a pressure exerted by the capsule against the restraint interior surface and to maintain the chamber at a substantially constant volume;  and

an energy source operable to supply sufficient thermal energy to the capsule so that the determined temperature is at least about 800 degrees Celsius, wherein the fluid is responsive to the thermal energy both to become supercritical at the determined temperature and at the substantially constant volume in the chamber, and to increase the pressure in the volume to at least the determined pressure.

Claim 105.  (Previously presented)  The apparatus as defined in claim 104, wherein the restraint is operable to counterbalance pressure in the capsule generated by the fluid in response to thermal energy, and the restraint is immobile relative to the capsule while counterbalancing the capsule pressure.

Claim 106. (Previously presented) The apparatus as defined in claim 104, further comprising a heating system that includes the energy source and a temperature sensor, wherein the temperature sensor is disposed proximate to the capsule and is operable to sense a temperature of the capsule.

Claims 107. – 111. (Cancelled)

Claim 112. (Previously presented) The apparatus of claim 104, further comprising a clamp in contact with the restraint, wherein the clamp is operable to reduce a pressure load on at least a portion of the restraint, and the pressure load can cause a longitudinal stress or an axial stress or both a longitudinal and an axial stress on the restraint portion.

Claims 113. – 129. (Cancelled)

Claim 130. (Previously presented) The apparatus as defined in claim 104, wherein the restraint is operable to transmit pressure to the capsule such that the transmitted pressure to the capsule is measurable as a pressure response of the restraint and is less than about 0.2.

Claim 131. – 144. (Cancelled)

Claim 145. (Previously presented) The apparatus as defined in claim 104, further comprising the fluid and the material, and wherein the fluid is sufficiently responsive to thermal energy to pressurize the capsule to an internal pressure in a range of greater than about 60 kbar, and the capsule and the restraint are cooperatively configured to maintain the seal at the internal pressure and at the corresponding temperature.

Claim 146. (Previously presented)  An apparatus, comprising:

a capsule having an interior surface defining a volume, the capsule having disposed within the volume an amount of metal material and an amount of ammonia, the capsule both is sealable to maintain an internal pressure, and is functionally capable of maintaining a seal to the amount of ammonia while the capsule is subject to a determined temperature and to a pressure in a range of from about 5 kBar to about 80 kBar;

a restraint having an interior surface defining a chamber that is configured to receive the capsule, and the restraint is responsive to resist a pressure exerted by the capsule against the restraint interior surface and to maintain the chamber at about a constant volume, and wherein the restraint is not operable to provide an active pressure load radially inward toward the capsule;  and

an energy source operable to supply thermal energy to the capsule, such that the ammonia responds to the thermal energy at the constant volume in the chamber to increase the pressure in the chamber and to become supercritical ammonia, wherein the supercritical ammonia reacts with the metal material to form a metal nitride composition.

Claim 147.  (Previously presented)  The apparatus as defined in claim 146, wherein the metal material comprises aluminum.

Claim 148.  (Previously presented)  The apparatus as defined in claim 147, wherein the restraint is capable of resisting the internal pressure, and the internal pressure is sufficiently high to form aluminum nitride.

Claim 149.  (Previously presented)  The apparatus as defined in claim 148, wherein the restraint is capable of resisting the pressure sufficient to form aluminum nitride at a temperature sufficient to form aluminum nitride.

Claim 150.  (Previously presented)  The apparatus as defined in claim 146, wherein, subsequent to use, the capsule has disposed in the volume the metal nitride composition.

Claim 151. (Previously presented)  The apparatus as defined in claim 150, wherein the capsule has disposed in the volume a single crystal metal nitride composition.

Claim 152. (Previously presented)  The apparatus as defined in claim 150, wherein the capsule has disposed in the volume aluminum nitride.

Claim 153. (Previously presented)  The apparatus as defined in claim 146, wherein the capsule is functionally capable of maintaining the seal to the amount of ammonia while the capsule is subject to the determined temperature and to the pressure in a range of from about 5 kBar to about 60 kBar.

Claim 154. (Previously presented)  The apparatus as defined in claim 112, wherein the clamp is operable to reduce the pressure load, and the pressure load can cause a longitudinal stress or both a longitudinal and an axial stress on the restraint portion.

Claim 155. (Previously presented)  The apparatus as defined in claim 104, further comprising the material and the fluid, wherein the material comprises aluminum, and the fluid comprises ammonia.

## Evidence Appendix II under 37 C.F.R. 41.37(c)(1)(ix)

The following pages include the references referred to in the argument and body of this Appeal Brief.

Included are:

Flanigen (US 3,567,643)

Wilson et al. (US 3,473,935)

Hall et al. (US 2,974,610)

## Related Proceedings Appendix III under 37 C.F.R. 41.37(c)(1)(x)

There are no related proceedings to this Appeal.

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ABSTRACT OF THE DISCLOSURE

A hydrothermal process for growing relatively large
macro-crystals having the structure of beryl. Growth takes
place on seed crystals from an acid medium which in-
cludes alkali metal and/or ammonium halides.

This application is a continuation-in-part of applica-
tion Ser. No. 646,121, filed June 14, 1967 which is in turn
a continuation of application Ser. No. 345,562, filed
Feb. 18, 1964 and now abandoned.

This invention relates to a process for growing crystals
having the structure of beryl. More particularly, it relates
to a process for growing large single crystals having the
structure of beryl of a size suitable for scientific and com-
mercial uses from seeds in acidic aqueous media at ele-
vated temperatures and pressures.

Beryl, which is the only ore of beryllium, is a crystal
having the ideal composition $3.0BeO \cdot 1.0Al_2O_3 \cdot 6.0SiO_2$,
and is commonly found in its natural form in granite. Its
crystal structure is a hexagonal system, and it is usually
found in the form of long, six-sided prisms. The frame-
work of the crystal structure of beryl is a complex cyclo-
silicate ring structure in which the silicon atoms are at
the centers of a group of four oxygen atoms lying at the
points of tetrahedra. These tetrahedral groups are linked
together by the sharing of oxygen atoms in the rings hav-
ing the composition $Si_6O_{18}$. The silica rings are joined to-
gether by aluminum atoms lying in the center of a group
of six oxygen atoms, and by berryillium atoms in a simi-
lar group of four oxygen atoms. There are two molecules
in each unit cell. Beryl ranges in Moh's hardness from 7.5
to 8, and in specific gravity from 2.63 to 2.85.

In addition to pure beryl, there are crystallographic
analogs of beryl which are also valuable for scientific and
commercial uses. The structure of these analogs is essen-
tially the same as that of beryl, except for the presence
of small amounts of materials other than the oxides of
beryllium, silicon and aluminum which are present. For
example, when small amounts of aluminum are isomor-
phously replaced by chromium in the beryl crystal struc-
ture, a green crystallographic analog of beryl is obtained
which has the essentially the same crystal structure of
beryl. The product thus obtained is commonly known as
emerald, although green gemstone emeralds do not neces-
sarily always contain chromium.

When a metal ion other than those of aluminum, silicon
and beryllium is incorporated in small amounts in the
structure of beryl, the crystal which is thus obtained is
commonly known in the art as a "doped" crystal. For
example, when small amounts of chromium are incor-
porated in the crystal structure of beryl, the resulting
emerald which is obtained could be considered to be a
"chromium-doped" beryl. The ion thus incorporated in the

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crystal structure is usually referred to as a "dopant ion."
For example, in the case of synthetically grown emerald
or "chromium-doped" beryl the chromium which is incor-
porated in the synthetic crystal would be considered to
be the "dopant" ion. Thus, the terms "doped" and "dop-
ant" are well-known in the are and are intended to have
the above defined and well known meanings whenever
they appear hereafter in this application.

In recent years there has been an increased interest in
the art of growing large synthetic crystals. Although ini-
tially this interest was stimulated by successes in growing
synthetic crystals for use in the gemstone art (for ex-
ample, synthetic ruby anud synthetic sapphire crystals,
etc.) more recent developments in the physics and chem-
istry of the solid state have created a demand for synthetic
crystals which may or may not also be of interest in the
field of solid state applications (for example, large syn-
thetic crystals of ruby or red corundum have been used
successfully in maser and laser applications).

Although there are several general types of processes
known for growing crystals (for example, the Verneuil or
flame-fusion process, and the Czochralski method of crys-
tallizing from a melt), these processes have inherent draw-
backs for growing large synthetic crystals of beryl and
beryl analogs. The two mentioned techniques are most
often applied to growth of less complex systems and to
crystals which melt congruently. The large thermal gradi-
ents which are inherent in these processes tend to induce
strain, particularly in crystals of large size. A third meth-
od of growing single crystals is by the flux-melt method.
The disadvantage which is ofen encountered in the flux-
melt method is the incorporation within the crystal growth
of the flux material or other undesirable impurities. By
the hydrothermal synthesis of single crystals having the
structure of beryl to be herein described, strain-free, high-
quality, optically transparent materials may be more read-
ily obtained; and the growth of relatively large synthetic
macro-crystals having the structure of beryl can be
achieved.

Although the hydrothermal process for crystal synthe-
sis is known in the art as a general technique used in
crystallization, the applicablility of this process depends
to a great extent on the particular type of crystal which
is being synthesized, the process conditions which are em-
ployed, and the compositions of the reactant mixture or
medium from which crystallization is being attempted.
The hydrothermal process of crystallization is generally
understood to a mean a process wherein an aqueous sol-
vent under high temperature and pressure is used to in-
crease the insolubility of reactants to a point at which
crystals of a material may be prepared. Much more diffi-
cult and unpredictable, however, is the application of hy-
drothermal techniques to the growth of single crystals of
any size in a controlled manner. An article by R. A. Lau-
dise in Progress in Inorganic Chemistry, vol. III, page 2
(1962) indicates that the utility of this process in pre-
paring a particular type of crystal depends on the discov-
ery of the proper set of conditions for crystal growth.
Predictive ability is poor, and a complex series of criteria
which may sometimes be mutually exclusive must be com-
promised before a single crystal can be grown. As fur-
ther proof of the unpredictability of applying the known
principles of the general process in an attempt to prepare
a particular crystal, E. J. Gubelin in an article in Gems
and Gemology, Winter 1960–1961, pp. 105–113, stated
that "solvent, nutrient, temperature, pressure and for-
eign agents are only a few of the variable factors that may
render the hydrothermal synthesis a hazardous gamble."

In the prior art there are some reference to hydrothermal processes for growing synthetic crystals having the structure of beryl, but none of these references teaches a satifactory method for growing synthetic crystals of beryl of any significant size. Although some of the hydrothermal methods for growing synthetic crystals of beryl structure which are known in the prior art give a general outline of the systems and conditions which were employed, most references to the prior art processes relating to crystals with beryl structure tend to be vague and highly speculative in nature.

In an article by G. Van Praagh entitled "Synthetic Quartz Crystals" which appeared in Geological Magazine, vol. 84, pp. 98–100 (1947), the author indicates that Professor R. Nacken of the Mineralogical Institute of Frankfurt University had some success in preparing synthetic crystals of emerald by a hydrothermal process. The process was apparently similar to his process for growing quartz, but the critical details of the process such as the specific mineralizers, nutrients and reaction conditions which were employed are not disclosed.

C. F. Chatham of San Francisco has been growing synthetic emeralds for commercial use in the gemstone field since 1935. Although the Chatham process has produced synthetic crystals of significant size and quality, the details of his process have also never been disclosed. Since Chatham first made his crystal products available to the art there has been a considerable amount of speculation by experts in the field as to the process which he employs, but details relating to the actual process are still unavailable at the present time. E. A. D. White in an article in Quarterly Reviews, vol. 15 (1961), pp. 1–29, hypothesized that Chatham's process was a hydrothermal process wherein crushed beryl was the nutrient, but details of the process were not given. Others have more recently suggested that the Chatham process is a flux-fusion process, and not the hydrothermal process that it was originally believed to be.

In addition to the Chatham synthetics discussed above, another emerald substitute which has recently appeared on the market is Lechleitner's "Emerita" stones. The details of the process used in preparing these stones have not been revealed, but these stones are apparently a product of a process wherein a thin synthetic emerald overgrowth or layer is applied to a relatively large faceted beryl seed. Gubelin has presented an hypothesis as to Lechleitner's process, indicating that this process may be analogous to Nacken's process for growing quartz, and that the synthesis of the emerald overgrowth is brought about in an alkaline medium under pressures of approximately 1000 atmospheres and at temperatures between 300 and 400° C. In contrast to Gubelin's hypothesis of Lechleitner's process, the work of Wyart and Scavnicar [Bull. Soc. franc, Miner Crist., LXXX, pp. 305–306 (1957)] indicated that the incorporation of trace amounts of $NaHCO_3$ to give a weakly alkaline medium did not improve their hydrothermal process for synthesizing micro-crystals of beryl, and that the presence of more than trace amounts of this alkali caused the formation of undesirable impurities such as albite and feldspar. Their attempts to dope their micro-crystals with chromium were inconclusive, since a number of undesirable impurities such as phenacite, quartz and chromium oxide were formed, and they were unable to determine if any chromium was actually incorporated into the micro-crystals which they obtained.

The principal object of the present invention is to provide a process for synthesizing single crystals having the structure of beryl, particularly beryl analogs doped with transition metal or rare earth metal ions.

Another object is to provide synthetic crystals of beryl structure, particularly those doped with transition metal or rare earth metal ions which are of a size suitable for use in the gemstone art and in solid-state devices.

Other and further objects and advantages of the present

invention and the preferred embodiments thereof will become apparent and are disclosed in detail in the following description.

The present invention relates to a hydrothermal process for growing single crystals having the structure of beryl which comprises depositing a composition having the structure of beryl on a seed crystal from an aqueous reactant mixture which comprises (1) at least a major amount of (A) sources of oxides of beryllium, aluminum and silicon and (B) an acidic halide medium which comprises at least one member selected from the class consisting of alkali metal halides and ammonium halides and (2) a minor amount of (C) sources of ions of at least one metal selected from the class consisting of transition metals and rare earth metals as a dopant, said process being operated at a temperature of at least 425° C. and under a pressure of at least 6000 pounds per square inch.

The transition metals useful in the process of this invention are those having atomic numbers from 21 through 28 inclusive; 39 through 46, inclusive; and 72 through 78 inclusive. The rare earth metals useful in the process of this invention are those having atomic numbers from 57 through 71, inclusive. A preferred group of transition metals comprises vanadium, chromium, manganese, iron, cobalt and nickel; these dopant elements impart highly desirable color characteristics to gemstone crystal products of this invention. A preferred group of rare earth metals comprises neodymium, samarium, gadolinium and europium because these dopant elements impart particularly desirable optical properties to crystals for use in solid state devices.

Since the process of this invention is a hydrothermal process which is conducted at elevated temperatures and pressures, the process is most easily conducted in a sealed reaction vessel, autoclave or bomb of a type well known in the hydrothermal art of crystal synthesis. A variety of these reaction vessels are commercially available and are highly suitable for use in practice of this invention. The reaction vessel which is employed should be constructed of a high strength, corrosion-resistant steel in order to withstand the pressures and temperatures encountered in the present process. One such suitable material is a nickel alloy of a high-strength, stainless steel. The reaction vessel may also be provided with a liner or capsule of a noble metal, such as silver, platinum or gold in order to avoid corrosion of the vessel by the acidic medium which is employed in the process of this invention. Several designs for high pressure reaction vessels are suitable for use in conducting the process of this invention, for example, those described by A. A. Ballman and R. A. Laudise ["Hydrothermal Growth," The Art and Science of Growing Crystals (1963), pp., 232–235], and a gold-lined or platinum-lined bomb similar to the that described by Morey in Amer. Miner., vol. 22, p. 1121 (1937). The bomb or capsule should remain tightly sealed throughout the reaction period in order to maintain the optimum conditions for satisfactory growth and crystal clarity.

The silicon, beryllium and aluminum oxide nutrients which are present in the aqueous acidic reactant mixture are usually present in the form of hydrous oxides of these metals. Any convenient source of the oxides of silicon may be employed as a starting material, such as for example, optical grade quartz crystal, fused quartz, $SiO_2$ porous glass and the like. The use of optical grade quartz crystal is preferred. Similarly as a source for the oxides of aluminum one may employ materials such as sapphire, gibbsite ($Al_2O_3 \cdot 3H_2O$), aluminum hydroxide which has been precipitated from solutions of aluminum salts such as aluminum nitrate and the like. Convenient sources of the oxides of beryllium are materials such as beryllium hydroxide [$Be(OH)_2$], beryllium oxide, and the like. Although the composition of the reactant mixture with respect to the oxides of silicon, beryllium and aluminum may vary over a wide range, a reactant mixture containing these oxides in amounts which closely ap-

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proximate the stoichiometric amount of these oxides in the composition of the ideal beryl crystal

$$(3.0BeO \cdot 1.0Al_2O_3 \cdot 6.0SiO_2)$$

is preferred.

When doped beryl crystals are prepared according to the present process, the source of the transition metal or rare earth metal ion dopant which is present in the reactant mixture is a metal compound such as a transition metal or rare earth hydroxide, a transition metal or rare earth metal nitrate, a transition metal or rare earth metal oxide, a transition metal or rare earth metal chloride, a transition metal or rare earth metal sulfate and the like. The source of the metal ion dopant may also be the reaction vessel itself. For example, in the case where an unlined, nickel-alloy, stainless steel reaction vessel is employed, the bomb material may supply ions such as iron and nickel ions.

Although it theoretically should be possible to incorporate over 10% by weight of a transition metal or a rare earth metal ion dopant into the beryl structure, lower weight percentages of dopant are normally incorporated into the beryl crystal by the process of this invention. Depending primarily on the requirements dictated by the particular end use of the crystal being grown, the concentration of transition metal or rare earth metal ion dopant in the crystal product may vary from about 0.005 weight percent to about 8 weight percent, based on the total weight of the crystal. 0.01 weight percent to 2 weight percent is preferred. When the dopant ion is chromium, a concentration of 0.1 to 2 weight percent is particularly preferred.

In order to provide an amount of transition metal or rare earth metal ion dopant sufficient to produce crystals containing dopants in amounts within the ranges of percentages set forth above, the reactant mixture should contain a metal ion concentration of from about 0.01 weight percent to about 11 weight percent, based on the weight of beryl equivalent to oxide in the nutrient of aluminum, silicon and beryllium in the initial charge. Preferably, the concentration of transition metal or rare earth metal ion from the compound is from 0.01 weight percent to 2 weight percent, based on the theoretical weight of beryl from the oxide sources. More than one transition metal or rare earth metal ion may be used simultaneously as a dopant in the initial charge.

Another essential component of the aqueous reactant mixture of the process of this invention is an acidic halide medium selected from the class consisting of alkali metal halide and an ammonium halide. In the absence of the acidic halide medium, little or no growth of crystals of beryl structure occurs. The preferred acidic halide media are alkali metal halides such as sodium chloride and ammonium halides such as ammonium chloride. The use of ammonium chloride is particularly preferred.

Although the concentration of the halide which is employed may be varied over a wide range, the limits of this concentration appear to be dependent on a number of factors such as the pressure and temperature at which the reaction is conducted, the over-all composition of the reactant mixture, the initial pH of the reactant mixture, and the halide which is employed. When ammonium chloride is employed, concentrations of less than 0.1 N ammonium chloride do not provide a satisfactory system. Concentrations of ammonium chloride as high as 11 N have been employed with good results. Systems which have provided highly satisfactory results are reactant mixtures containing 1 N to 7 N ammonium chloride. Mixtures containing 5 N ammonium chloride are particularly preferred.

In addition to the presence of the necessary halide, it is essential to practicing the process of this invention to provide a reactant mixture which initially has a pH at 25° C. of less than 7. Although an initial pH of from

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0.2 to 4.5 is preferred, the pH has been found to be somewhat dependent on the temperature at which the reaction is conducted. At a temperature of 500° C. the growth rate decreases considerably when the initial pH at 25° C. is appreciably below 3, and the crystals which are cloudy and of poor quality are obtained when the initial pH at 25° C. is above 5. However, when the reaction temperature is increased to 600° C., for example good growth rates were observed and high quality crystals were obtained at initial pH's at 25° C. which were as low as 0.2.

When the source of the transition metal ion dopant or the rare earth metal ion dopant is an ionic material which readily hydrolyzes in solution to provide an acidic mixture, further adjustment of the pH may not be necessary. For example, when a sufficient amount of the hydrate of chromic chloride is employed as a source of chromium ion dopant, the hydrolysis of the chromic chloride and the ammonium chloride which is present are usually sufficient to provide a pH within the preferred range set forth above. The pH of the reaction mixture may be adjusted with a mineral acid such as HCl in an amount sufficient to provide a pH within the desired range.

It has also been found that when chromium is being used as the dopant ion, it is highly desirable that the acidic aqueous reactant mixture should be substantially free of fluoride ion, in order to avoid precipitation of metal fluorides such as chromium fluoride which are insoluble and form precipitates under the acidic conditions of the present process. The presence of insoluble metal fluoride salts causes inclusions and cloudiness in the resulting crystals which are obtained, hinders the incorporation of the chromium ion dopant into the crystal except as occluded particles, and affects the rate of growth adversely.

In practicing the process of the present invention the synthetic beryl or doped beryl is grown on a seen crystal located within the sealed reaction vessel. The nutrient oxides and dopant ions migrate to the region of the seed, and new growth crystallizes thereon. Although any crystal having the structure of beryl or other suitable substrate may be used as a seed, a seed crystal of natural or synthetic beryl or a beryl analog is usually employed. Normally, the reaction is continued until the new growth is thick enough to be cut from the original seed. This new growth may then be employed as a seed crystal in further subsequent reactions. In this way macro-crystals of beryl structure of only synthetic hydrothermal origin are obtained. This is particularly useful in preparing macro-crystals of beryl structure having high purity and uniform composition and structure. Large synthetic crystals may also be obtained by conducting a series of short-term runs wherein fresh oxide nutrient and solution are used in each run of the series. A highly favorable aspect of this invention is the ability to achieve and maintain favorable growth rates over extended periods of time. For example, an average growth rate of greater than 0.2 mm. per day in the length of an edge of a crystal has been maintained over a period of 5 days, and an average of as high as 0.1 mm. per day has been maintained over a period of 30 days.

Another favorable aspect of this invention is the ability to substantially confine growth of crystal having the structure of beryl to the seed, and to obtain single crystal growth on said seed or seeds which is substantially flawless and optically transparent. Spontaneous nucleation and twinning on the surface of the seed are eliminated.

Although the condition of the surface of the seed crystal which is employed may influence the rate of growth of new material on the seed, it has been found that the rate of growth on the sawed faces of a seed crystal is about the same and in some instances better than the rate of growth observed on a fractured face of a seed crystal. However, the growth rate is somewhat dependent on the axial orientation of the seed face upon which the

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new growth is being deposited and the oxide sources which are being employed. When powdered beryllium hydroxide and powdered aluminum hydroxide are employed, growth is fastest on faces cut at approximately 45° to the crystallographic c-axis, and the rate of growth decreases as the face approaches a position parallel to the c-axis or a position perpendicular to the c-axis. Favorable growth rates are obtained on faces cut within the range of 10° to 60° of the c-axis. Using the process of this invention, growth rates of greater than 0.2 mm. per day in the length of an edge of the crystal have been achieved.

The present process for growing crystals having the structure of beryl is conducted at temperatures of from about 425° C. to about 800° C. and at pressures of from about 6000 pounds per square inch to about 30,000 pounds per square inch. Although it may be difficult to determine with absolute accuracy the actual operating pressure for the high-pressure systems employed in the present process, the internal pressure within the reaction vessel can be calculated from known pressure-temperature-volume data on water when low concentrations of solutes are present. Knowing the volume of the reaction vessel, the volume of the reactant mixture and the reaction temperature, the reaction pressure can be most conveniently calculated by using the pressure-temperature-volume data for pure water published by G. C. Kennedy in American Journal of Science, vol. 248, p. 540 (1950). However, since the presence of high concentrations of solutes lowers the pressure of the system somewhat from that of pure water, the effect of 5 N NH$_4$Cl was determined by making actual measurements at various temperatures using small bombs which contained a 5 N NH$_4$Cl solution. The following table lists several corrected values for two percentages of fill:

| | Corrected pressure in pounds per square inch at 62% fill | Corrected pressure in pounds per square inch at 73.5% fill |
|---|---|---|
| Temperature in degrees centigrade: | | |
| 417 | | 6,370 |
| 423 | 5,290 | |
| 447 | | 8,670 |
| 464 | 7,260 | |
| 473 | | 11,350 |
| 497 | 9,780 | |
| 508 | | 15,750 |
| 538 | | 20,400 |
| 555 | 14,900 | |
| 621 | 20,800 | |

It should also be understood that the upper limits of temperature range and particularly the pressure range are dependent to a great degree on the equipment which is available, and that these upper limits might be extended if equipment could be designed to withstand the higher temperatures and pressures. With the equipment which is presently available, the reaction temperature is from abount 425° C. to about 800° C., and the pressure is from about 6000 pounds per square inch to about 30,000 pounds per square inch. A temperature of from 475° C. to 650° C. and a pressure from 9000 pounds per square inch to 21,000 pounds per square inch is preferred.

It has also been found that the growth rate may be accelerated somewhat by maintaining a temperature differential between the upper and lower portions of the reaction vessel or bomb. This differential may be achieved by providing a separate heating element for the lower portion of the reaction vessel or bomb, and then positioning the reaction vessel and the heating element in a large furnace which is maintained at a temperature which is lower than that produced by the heating element. In this manner, a temperature differential is easily maintained by suitable control of the bomb and the furnace heaters. A temperature differential between the top and the bottom of the reaction vessel of from about 10° C. to

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about 100° C. may be employed. A differential of from 10° C. to about 20° C. is preferred.

It has also been found that the rate of growth may be affected by the geometry of the seed crystal and the oxide nutrient sources within the reaction vessel. For best results the seed crystal should be positioned at a point in the reaction vessel which is intermediate to the zone wherein the silica source is located and zone wherein the beryllium oxide and aluminum oxide sources are located. Throughout the reaction the seed crystal and all of the oxide sources are in intimate contact with the acidic aqueous reactant mixture. The relative distances between the silicon oxide source, the seed crystal or crystals, and the beryllium and aluminum oxide sources have not been found to be critical. An arrangement which has been found to be highly suitable for growing single crystals or good quality at relatively high growth rates is one in which the oxide sources of beryllium oxide and aluminum oxide are placed at the bottom of the reaction vessel, the silicon oxide source is suspended by means of a wire or a porous gauze basket of noble metal in the upper portion of the reaction vessel, and the seed crystal or seed crystals are suspended by means of a noble metal wire at a point in between.

It is also possible to employ multiple groups of oxide sources and seed crystals within a reaction vessel wherein individual sets of oxide sources and seeds are "stacked" in separate arrangements within said vessel and all are in contact with a common acidic aqueous reactant mixture. The number of sets which may be employed is determined primarily by the available volume of the reaction vessel. The "stacked" system is not a preferred method for carrying out the process of this invention.

When crystals prepared according to the process of this invention are removed from the reaction vessel after it has cooled, the surfaces of these crystals may be covered with other phases or impurities which formed within the autoclave during cooling. Although these phases or impurities are not substantial in quantity, any impurities may be removed before use of the crystal product as a gemstone or in a solid-state device by washing with hot or cold dilute acid solutions and water or by scraping the surfaces clean.

An analysis of a typical sample of a chromium-doped beryl product prepared by the process of this invention is as follows:

| | Wt., percent | Moles |
|---|---|---|
| SiO$_2$ | 64.9±0.5 | 6.51 |
| Al$_2$O$_3$ | 16.9±0.3 | 1.00 |
| BeO | 15.0±0.5 | 3.62 |
| H$_2$O | 1.0±0.5 | 0.34 |
| Cr | 1.07 | 0.12 |

Typically, several other single crystals of chromium-doped beryls prepared by the process of this invention were found to contain 0.26%, 1.1% and 1.07% by weight of Cr.

The crystals prepared by the process of this invention were found to differ from the ideal stoichiometry for beryl, 3.0BeO·1.0Al$_2$O$_3$·6.0SiO$_2$, as can be seen from the typical analysis set forth above.

Properties of the chromium-doped crystals prepared by the process of this invention have been found to differ significantly from those reported in the literature for chromium-doped beryls such as natural emeralds and synthetic emeralds. By comparing all of the properties shown in the accompanying Table I for natural and synthetic emeralds with those of the chromium-doped beryl crystals of this invention, one can readily distinguish crystals of this invention from both natural emeralds and synthetic emeralds.

TABLE I.—COMPARISON OF PROPERTIES OF CRYSTALS

| Crystal | Specific gravity | Mean refractive indices | Fluorescence behavior | | Intensity through Chelsea filter [3] | |
|---|---|---|---|---|---|---|
| | | | Long wave [1] U.V. | Short wave [2] U.V. | Low scale | High scale |
| Natural emeralds | 2.69-2.77 | 1.57-1.58 | None to pale red to red | None to pale red | N.D. | N.D. |
| Natural Columbian emerald (0.2% Cr) | 2.70 | 1.57 | None to pale red | do | <2 | N.D. |
| Chatham synthetic emerald | 2.65-2.66 | 1.56 | Deep red | Deep red | 8-14 | 39 |
| Lechleitner synthetic emerald overlay on a Brazilian beryl ("Emerita") | 2.65-2.71 | 1.58 | Pale red to red | Pale red to red | 8 | 11 |
| Cr-doped beryl of this invention | 2.66-2.71 | 1.57-1.58 | Brilliant red | Brilliant red | | |
| (a) Rough, 1.0% Cr | | | | | 19-30 | 76-120 |
| (b) Rough, 0.8% | | | | | 13-25 | N.D. |
| (c) Faceted stone, 1% Cr | | | | | 25 | 42-62 |
| Synthetic ruby (0.05% Cr) | 4.0 | 1.77 | Brilliant red | Brilliant red | N.D. | 270-300 |

[1] 3,650 A.
[2] 2,537 A.
[3] Chelsea filter: A dichromatic filter, transmitting in the deep red near 6,900 A., and in the yellow-green near 5,400 A., used to distinguish emeralds; see R. Webster, "Gems," vol. II, Butterworths, p. 570 (1962). The exciting radiation was an ultraviolet lamp, 2,537 A.; fluorescence intensity was measured with pinhole optics, normal to direction of exciting beam, through Chelsea filter, detected with photomultiplier tube in microdensitometer apparatus; apparatus; approximate incident radiation intensity of U.V. lamp was 50 milliwatts/sq. ft.
NOTE.—N.D.=Not determined.

For example, although natural emeralds exhibit values of refractive index and specific gravity similar to those of Cr-doped beryl crystals of this invention, the fluorescence behavior of the former is significantly different from that of the latter. Similarly, although the synthetic Chatham emerald (believed to be a flux-grown material) shows a strong fluorescent intensity, Cr-doped beryl crystals of this invention can readily be distinguished from the Chatham product on the basis of the respective refractive index and specific gravity values. It has been found that the fluorescence behavior of Cr-doped crystals of this invention is a particularly distinguishing characteristic thereof. As can be seen from Table I, the relative fluorescence intensity values, measured through the Chelsea filter, for Cr-doped beryl crystals of this invention are as much as about ten times as large as those values measured for the natural and synthetic emeralds listed. Also on a visual basis under the radiation from a standard laboratory ultraviolet lamp (long or short wavelength) Cr-doped beryl crystals of this invention exhibited a distinct brilliant red fluorescence substantially more intense than the fluorescence level exhibited by the natural and other synthetic emeralds tested. This fluorescence can also be excited by incident radiation in the visible violet and blue region. Differences in refractive index, specific gravity and fluorescence behavior are means readily recognized and used by those skilled in the art to distinguish crystals, particularly in the field of gemstones and solid state materials. By way of comparison, Table I also includes data on the fluorescence behavior of a ruby crystal. Ruby exhibits the most intense red fluorescence of all known crystals, and such behavior is usually indicative of a utility in solid state applications, as in a laser device. It is seen that the fluorescence intensity values for Cr-doped beryl crystals of this invention are surprisingly good in relation to the value listed for ruby.

Another distinguishing characteristic of the crystals produced by the process of this invention is their infrared spectrum. All of the crystals produced by the present process are characterized by a strong absorption band in the OH-strength region near 3700 reciprocal centimeters and the absence of a strong band in either of the absorption region (a) near 3600 reciprocal centimeters and (b) between about 1600 and about 1650 reciprocal centimeters. The infrared spectra of the crystals of this invention are measured by conventional techniques employed on powdered solids, for example, KBr wafer or mull methods. This characteristic infrared spectrum makes it possible to distinguish crystals produced by the process of this invention from natural beryl and beryl analogs. For example, natural emeralds also show a strong absorption band at 3700 cm.$^{-1}$ but, in addition, have a strong band between 1600 and 1650 cm.$^{-1}$ and often a strong band near 3600 cm.$^{-1}$.

The crystals of this invention can also be distinguished from any type of flux grown beryl or beryl analog be-

cause the crystals of this invention have high quality and a lack of flux inclusions, and because flux-grown beryl and beryl analogs have infrared spectra devoid of any significant absorption bands characteristic of hydroxyl groups. Additional distinguishing properties are refractive index, birefringence and specific gravity as shown in the following Table II.

TABLE II

| | Flux-grown chromium-doped beryl | Hydrothermal grown chromium-doped beryl |
|---|---|---|
| Refractive index range | 1.56-1.57 | 1.57-1.58 |
| Birefringence | 0.003-0.005 | .005-0.006 |
| Specific gravity | 2.66-2.67 | 2.66-2.71 |

The process of this invention typically produces tabular shaped crystals bounded by dipyramid and prism faces. Natural and flux-grown beryl and doped beryl crystals have the shape of hexagonal prisms. This difference in morphology is believed to be caused by variation in growth rate along specific crystallographic directions.

Thus, the combination of chemical and physical properties of the crystals of this invention, including size, optical quality, infrared spectrum, fluorescence characteristics, specific gravity and refractive index, make it possible to distinguish crystals of this invention from natural beryl and its natural analogs and from other synthetic beryls and beryl analogs.

A particular advantage of the single crystals of beryl structure of this invention is the utility of the doped crystals in solid-state applications. Such applications often require that the crystal be free of crystal imperfections and contain only a controlled amount of dopant ion or ions homogeneously distributed throughout the crystal structure and be substantially free of undesirable extraneous impurities, such as flux inclusions. Naturally-occurring crystals of beryl structure such as emeralds almost always contain at least small amounts of several impurity ions. In addition, the level of extraneous ions is often considerably out of the range desired for solid-state applications.

Following are examples of the practice of the invention which is hereinbefore described.

EXAMPLE I

0.36 gram of gibbsite ($Al_2O_3 \cdot 3H_2O$) and 0.31 gram of powdered beryllium hydroxide were placed at the bottom of a gold-lined reaction vessel, and 0.90 gram of crushed quartz crystal were suspended in a platinum bucket in the upper portion of the vessel. 0.273 gram of $CrCl_3 \cdot 6H_2O$ was added to provide chromium ion dopant, and two natural beryl seed crystals weighing 0.1695 gram and 0.0651 gram were suspended in the reaction vessel between the silica source, and the alumina beryllia source. The vessel was then filled to 62% of its capacity with 9.3 cc. of an aqueous solution of 0.1 N $NH_4Cl$ and 0.1 N

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NH$_4$OH. The initial pH of the resulting reactant mixture was 2.85 at 25° C. The reaction vessel was sealed, and an auxiliary furnace was attached to the bottom of the reaction vessel in order to maintain a temperature differential between the top and the bottom of said vessel. The vessel with the auxiliary furnace attached was placed in a larger furnace and heated to 475° C. The top of the reaction vessel was maintained at a temperature of 475° C. while the bottom of the vessel was maintained at a temperature of 500° C. through use of the auxiliary heater which was attached. The resultant pressure within the reaction vessel was approximately 20,000 pounds per square inch. After six days the vessel was removed from the larger furnace, quenched with water until cool, and opened. The seed crystals were removed from the reaction vessel, washed, and dried. Upon weighing, the seed crystals were found to have gained 9.2% and 6.0% respectively in weight. The new growth was clear green in color (about 2 wt.-percent Cr) and examination of this new growth under high magnification indicated that chromium had entered the crystal as a structural component. Measurements of the new growth showed average linear growth rates in an edge of a crystal 0.019 mm. per day and 0.010 mm. per day, respectively.

### EXAMPLE II

0.53 gram of gibbsite, 0.46 gram of powdered beryllium hydroxide, 1.43 grams of crushed optical quartz crystal, and 0.41 gram of CrCl$_3$·6H$_2$O were placed in a gold-lined reaction vessel in a manner similar to that set forth in Example I. Four seed crystals of natural beryl ranging in weight from 0.0800 to 0.1157 gram were suspended between the quartz and the gibbsite-beryllium hydroxide mixture, and the vessel was filled in 62% of its capacity with 9.3 cc. of an aqueous solution of 0.1 N NH$_4$Cl and 0.1 N NH$_4$OH. The initial pH of the resulting reactant mixture was 2.8 at 25° C. the reaction vessel was sealed, placed in a furnace, and heated to 500° C., at which the internal pressure was 20,000 pounds per square inch. After 6 days the vessel was removed from the furnace, quenched until cool, and opened. The seeds had gained from 8.0 to 21.9% in weight and the average linear growth rates ranged from 0.013 to 0.035 mm. per day. The quality of the new green growth (about 2% Cr) was considered excellent.

### EXAMPLE III

In order to illustrate the deleterious effect of the presence of fluoride ion when the dopant ion is chromium, a reactant mixture similar to that in Example II was prepared, except that a solution of 0.1 N NH$_4$F and 0.1 N NH$_4$OH was used instead of a solution of 0.1 N NH$_4$Cl and 0.1 N NH$_4$OH. The initial pH of this reactant mixture was 4.3 at 25° C. After 4 days at 510° C. green growth was observed on all four seeds, but microscopic examination revealed that the new growth was spoiled by numerous inclusions of solid, powderous green particles of CrF$_3$ which was insoluble in the acid medium.

### EXAMPLE IV

1.06 grams of powdered aluminum hydroxide, 0.92 gram of powdered beryllium hydroxide, 3.0 grams of crushed crystal quartz and 0.04 gram of CrCl$_3$·6H$_2$O were placed in a gold-lined reaction vessel in an arrangement similar to that of Example II. Four beryl seed crystals were suspended between the silica source and the alumina-beryllia source, and 8.2 cc. of an aqueous solution of 1.0 N NH$_4$Cl were added. The initial pH of the resulting reactant mixture was 3.7 at 25° C. After 3.5 days at 520° C. and approximately 20,000 pounds per square inch pressure, the seed crystals exhibited an increase in weight of from 7.4% to 14.0%. The average linear growth rates ranged from 0.020 to 0.034 mm. per day, and the quality of the new growth (about 0.2 weight percent Cr) was considered to be excellent.

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### EXAMPLE V

Example IV was repeated using a 5.0 N NH$_4$Cl solution in place of the 1.0 N NH$_4$Cl solution and three beryl seed crystals instead of four. Initial pH of the reactant mixture was 4.1 at 25° C. Over an 8.5 day period at 515° C. and approximately 12,000 pounds per square inch pressure, the seeds grew at an average linear growth rate of 0.045, 0.046 and 0.052 mm. per day. The new growth (about 0.2 weight percent Cr) was considered to be excellent.

### EXAMPLE VI

In a procedure similar to that of Example IV growth was obtained on four beryl seed crystals weighing from 0.024 to 0.104 gram. 1.06 grams of powdered aluminum hydroxide, 0.92 gram of powdered beryllium hydroxide, 3.0 grams of crushed crystal quartz, and 0.06 gram of chromic chloride hydrate were employed, and the reaction vessel was filled to 62% of its volume with 8.93 cc. of a 5 N NH$_4$Cl solution. The initial pH of the resulting reactant mixture was 3.9 at 25° C. An average reaction temperature of 585° C. was maintained over a five day period. After five days, clear green growth had occurred on all seeds, at average linear growth rates of from 0.112 to 0.322 mm. per day. The quality of the new growth (about 0.3 weight percent Cr) was excellent.

### EXAMPLE VII

Example VI was repeated using 7.5 cc. of a 5 N NH$_4$Cl solution to obtain a 52% fill, and the chromium dopant source of CrCl$_3$·6H$_2$O was increased by a factor of five (0.3 gram of CrCl$_3$·6H$_2$O was used). The initial pH of the resultant reactant mixture was 2.7 at 25° C. A reaction temperature of from 590° C. to 620° C. was maintained over a five day period. After five days, a new growth of excellent quality but of a deeper shade of green (about 1.1 weight percent Cr) than that of the previous example was obtained. The average linear growth rate was 0.13 mm. per day.

### EXAMPLE VIII

In this run the bomb was of the lens-ring sealed type fabricated from Inconel-X (51.5 cc. volume). A gold crucible (22.4 cc. volume) with screw-on silver caps was used to prevent contamination of the crystal product. The charge consisted of 2.90 grams of aluminum hydroxide, 2.4 grams of beryllium hydroxide, 4.4 grams of crystal quartz and 0.1 gram of FeCl$_3$·6H$_2$O as the dopant. This nutrient medium was equivalent to 10 grams of beryl with 0.2% Fe. Four beryl seeds, two of which were cut at an angle to the c-axis and two cut at 90°, were used. The hydrothermal medium was 11.0 cc. of 0.1 N NH$_4$Cl. The initial pH of the resulting reactant mixture was 3.1 at 25° C. After 6 days at 500° C. and about 20,000 p.s.i. pressure, the bomb was cooled and opened. Growth rates ranging from 0.008 to 0.015 mm./day were measured. Growth of new iron-containing beryl was especially smooth on the prism-cut seeds.

### EXAMPLE IX

1.06 g. of aluminum hydroxide, 0.92 cc. of beryllium hydroxide and 0.18 g. of FeCl$_3$·6H$_2$O was placed in the bottom of a Morey bomb and 3.0 g. of crystal quartz in the top. Four seeds varying between .042 and .13 g. were suspended between the oxide nutrients. The bomb was loaded to 55% of fill with 7.9 cc. of 5 N NH$_4$Cl. The initial pH of the resulting reactant mixture was 2.9 at 25° C. The bomb was sealed and heated at 600° C. and 15,000 p.s.i. pressure for 5 days. The seeds grew at rates between 0.02 and 0.04 mm./day and an analysis of the crystal with its growth layers showed 0.21% Fe.

### EXAMPLE X

In a procedure similar to Example IX, the reactant mixture contained 1.06 g. aluminum hydroxide, 0.92 g.

beryllium hydroxide, 3.0 grams of crystal quartz and $NdCl_3$ (0.01% Nd) as the dopant. 8.8 cc. of 5 N $NH_4Cl$ was added. The pH of the resulting reactant mixture was 5.6 at 25° C. The mixture was adjusted to a final initial pH of 1.65 at 25° C. with 1 N HCl. The sealed bomb was heated at an average temperature of 520° C. for 7 days. The neodymium containing beryl growth on the seeds occurred at a rate between .001 and .007 mm./day.

### EXAMPLE XI

8.7 g. of gibbsite, 7.2 g. of berryllium hydroxide, 20.1 grams of crystal quartz and 0.31 g. of $CrCl_3 \cdot 6H_2O$ were placed in a gold crucible together with 27.6 cc. of 20% NaCl solution as hydrothermal medium. Four seeds ranging between 0.028 and 0.334 gram were suspended in the middle of the crucible. The initial pH of the resulting reactant mixture was about 4 at 25° C. The gold crucible was placed in a 150 cc. stainless steel bomb and 37.3 cc. of water added to balance the pressure within the crucible. The sealed bomb was heated at an average temperature of 620° C. for 5.5 days. Chromium containing growth occurred on the seeds at a rate between .004 and .007 mm. per day.

### EXAMPLE XII

In a procedure similar to Example IX 1.06 g. of aluminum hydroxide, 0.92 g. of beryllium hydroxide and 0.24 g. of $CrCl_3 \cdot 6H_2O$ was placed in the bottom and 3.00 g. of crystal quartz in the top of a gold lined Morey bomb. Four seeds ranging between 0.20 and 0.33 gram were suspended between the oxide nutrients. 7.2 cc. of 5 N $NH_4Cl$ was added. The initial pH of the resulting reactant mixture was 2.8 at 25° C. The sealed bomb was heated at 605° bottom and 590° top for a 30 day period. Pressure was about 13,500 p.s.i. All seeds grew at about 0.1 mm. per day and approximately 87% of the nutrient was converted to new crystal on the seeds. Analysis of the new chromium containing growth showed 1.1% Cr.

### EXAMPLE XIII

A gold crucible was charged with 2.9 g. of aluminum hydroxide, 2.4 g. of beryllium hydroxide, 4.4 g. of crystal quartz, 0.10 g. of $FeCl_3 \cdot 6H_2O$ and 11.0 cc. of 0.1 N $NH_4F$ in 0.1 N $NH_4OH$. Four seeds weighing between 0.077 g. and 0.081 gram were suspended in the center. The crucible was fitted with a gold screw on cap and loaded into an Inconel X bomb together with 12.0 cc. of water to balance the pressure. The initial pH of the resulting reactant mixture was 3.9 at 25° C. After sealing, this bomb was heated at 520° C. average temperature for 10 days. Growth rates ranging between .003 and .008 mm. per day were observed for the iron containing new growth.

### EXAMPLE XIV

Following the procedures of Examples IX and XII and using both $FeCl_3 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ as sources of dopant ions, the process of this invention gave new growth on seed crystals. Analysis showed the new growth to be high quality doped beryl containing 0.12 weight percent iron and 0.35 weight percent chromium.

Starting with as-grown (i.e. "rough") Cr-doped crystals weighing 1.14 grams and 0.78 gram produced according to the invention, two faceted gems weighing 0.5 carat (0.1 gram) and 0.4 carat (0.08 gram) were cut in a step-faceted style. These faceted gemstones were optically clear and exhibited a brilliant dark emerald-green color.

Chromium-doped beryl crystals of this invention are of a size and quality ideally suited for use in solid-state devices such as lasers and masers. F. E. Goodwin [Journal Applied Physics, 32, 1624–1625, (1961)] reported the successful operation of synthetic emeralds in a single-cavity reflection-type maser amplifier operating at 10 kmc. Goodwin noted that his synthetic emeralds "ex-

hibited a number of imperfections, as was evidenced by microscopic twinning and spontaneous nuclei." He speculated that crystals "relatively free of polycrystalline defects . . . will exhibit narrower line widths and superior maser characteristics." The high degree of single-crystal character and other crystal perfection of the Cr-doped beryl crystals of this invention are capable of providing such desired superior maser characteristics.

Though superior embodiments have been shown and described, it is to be understood that they are illustrative only, and are not to be construed as limiting the scope and spirit of this invention.

What is claimed is:

1. A hydrothermal process for growing single crystals having the structure of beryl which comprises: depositing a composition having the structure of beryl on a seed crystal from an acidic aqueous reactant mixture having an initial pH at 25° C. not above 5 and consisting essentially of: (1) at least a major amount of (a) sources of oxides of beryllium, aluminum and silicon, and (b) a halide solvent medium which consists essentially of water and at least one or more alkali metal halides and/or ammonium halides, and (2) minor amounts of sources of one or more of the dopant metals vanadium, chromium, manganese, iron, cobalt, nickel, neodymium, samarium, gadolinium and europium; said process being carried out at a temperature of at least 425° C. and under a pressure of at least 6000 pounds per square inch.

2. The process in accordance with claim 1 wherein said dopant metal is chromium.

3. The process in accordance with claim 1 wherein said sources of oxides of beryllium, aluminum and silicon are present in amounts which provide substantially the stoichiometric amounts of beryllium, aluminum and silicon oxides in the composition of an ideal beryl crystal (3.0 $BeO \cdot 1.0Al_2O_3 \cdot 6.0SiO_2$).

4. The process in accordance with claim 1 wherein said dopant metal is chromium and said aqueous reactant mixture is substantially free from fluoride ion.

5. The process in accordance with claim 1 wherein said aqueous reactant mixture has an initial pH at 25° C. of from 0.2 to 4.5 and in which said halide is ammonium chloride.

6. The process in accordance with claim 3 wherein (1) said sources of oxides of beryllium and aluminum are disposed near the bottom of a closed reaction vessel, said sources of oxides of silicon are disposed near the top of said vessel, and said seed crystal has the structure of beryl and is supported between said sources of oxides of beryllium and aluminum and said sources of oxides of silicon, and (2) wherein the temperature at the bottom of said reaction vessel is at least 10° C. higher than the temperature at the top of said vessel.

7. The process in accordance with claim 5 wherein said aqueous reactant mixture is substantially free from fluoride ion and wherein said source of dopant metal is $CrCl_3 \cdot 6H_2O$ which is present in said reactant mixture in sufficient amount to supply from 0.01 to 2 weight percent chromium ion in said crystal based on the weight of ideal beryl crystal theoretically equivalent to the weight of aluminum, beryllium and silicon oxides present in said oxide sources.

8. The process in accordance with claim 7 wherein said source of beryllium oxide is powdered beryllium hydroxide, said source of aluminum oxide is powdered aluminum hydroxide, said source of silicon oxide is crushed quartz, said halide solvent medium is 5 N ammonium chloride, and wherein the temperature at the bottom of the vessel is between 475° C. and 650° C. and the pressure is between 9000 and 21,000 pounds per square inch.

9. The process in accordance with claim 8 in which said seed crystal has a face cut thereon within an angle of from 10° to 60° with the c-axis of the crystal.

(References on following page)

**15**

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J. COOPER, Assistant Examiner

U.S. Cl. X.R.

23—110, 301, 305; 106—42; 252—62.59, 62.62, 301.4F

# UNITED STATES PATENT OFFICE
## CERTIFICATE OF CORRECTION

Patent No. _____ 3,567,643 _____ Dated _____ March 2, 1971 _____

Inventor(s) _____ E. M. Flanigen and N. R. Mumbach _____

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 58, delete "the", first occurrence.

Column 2, line 6, change "are" first occurrence, to

-- art --.

Column 2, line 49, delete "a".

Column 4, line 53, delete "the".

Table I, fourth line of footnote 3, delete

"apparatus".

Column 9, line 60, change "strength" to -- stretch --

Column 14, line 9, change "superior" to -- specific --

Column 14, line 54 (first line of claim 7), change

"5" to -- 6 --.

Signed and sealed this 20th day of July 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents
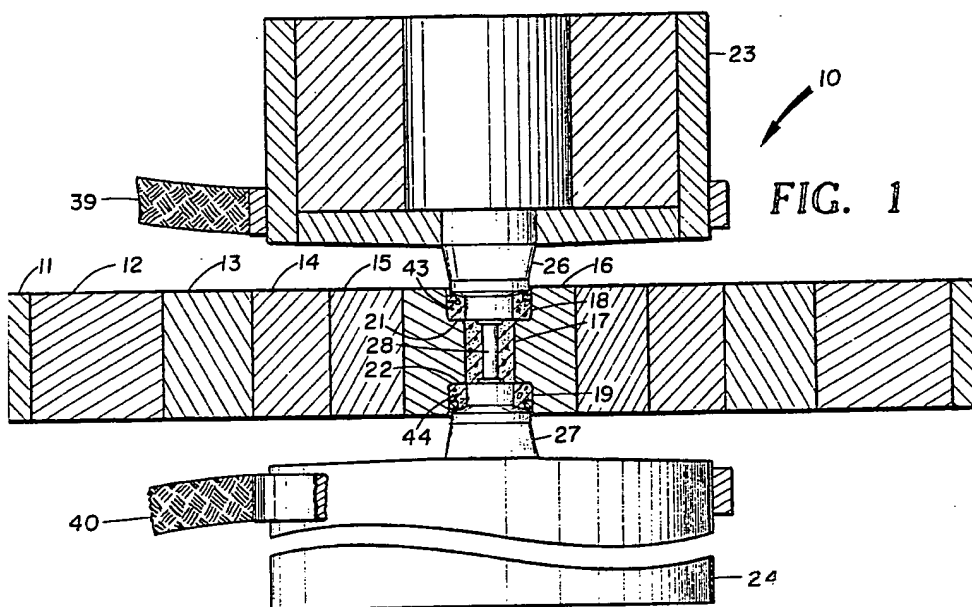
FIG. 1
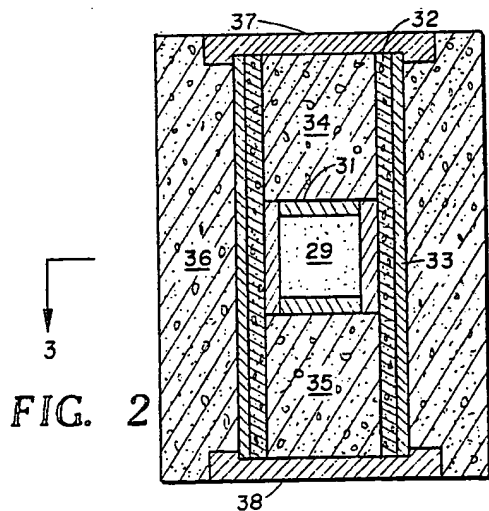


FIG. 2

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## ABSTRACT OF THE DISCLOSURE

A method of making beryl crystals by compressing
beryl powder at 7.5 to 15 kilobars at the melting tempera-
ture of beryl. The melting temperature may be lowered
by the use of a flux such as water or a fluorine source.

The invention described herein may be manufactured
and used by or for the Government of the United States
of America for governmental purposes without the pay-
ment of any royalties thereon or therefor.

This application is a continuation-in-part of applica-
tion Ser. No. 377,781 filed June 24, 1964, for Synthesis
of Beryl, now abandoned.

This invention pertains to the formation of crystalline
materials and more particularly to a method for pro-
ducing beryl crystals.

Beryl crystals have previously been formed by several
different methods each of which has its own peculiar
disadvantages. The growth of single crystals from a seed
crystal suspended in a melt suffers from the disadvantage
that it requires too long a time (probably in the order of
a week or more to produce a sizeable crystal) and the
Verneiul flame fusion process, although requiring less
time, suffers from the disadvantage that it is difficult to
maintain the necessary precise control over the feed rate
of the constituents employed. Moreover when these proc-
esses have been employed for the production of emerald
crystals, the emeralds produced have a density of 2.67 or
lower, which is considerably lower than the density of
natural emerald (2.70 and slightly higher than 2.71 for
the purest natural emerald). These synthetic emeralds
also have a series of wisp-like inclusions which are visible
to the naked eye and such inclusions seriously affect the
optical applications of the crystals.

Accordingly, it is an object of this invention to pro-
vide a new method for producing beryl crystals.

It is another object to produce clear single beryl crystals
in a short space of time.

It is a further object to produce single clear emerald
crystals.

It is still another object to produce emerald crystals
that have density, hardness and optical properties that
are superior to previous synthetic emeralds.

These and many other objects will become more fully
apparent from the following detailed description of the
invention wherein:

FIG. 1 is a partial cross-sectional view of a stepped-
core pressure apparatus for providing the high pressure
necessary to the present invention, the capsule containing
the material to be crystallized being shown in place; and

FIG. 2 is a cross-sectional showing of the capsule
itself.

The objects of this invention are accomplished by
forming beryl crystals under pressure from either beryl
powder or the constituents of beryl in their proper pro-
portions ($3BeO:Al_2O_3:6\ SiO_2$ which combine under the
process conditions to form beryl). It is to be understood
that the term beryl powder is meant to include all mem-

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bers of the beryl family which includes aquamarine (fer-
rous ion impurity), morganite (lithium ion impurity),
emerald (chromium ion impurity), golden beryl (ferric
ion impurity) and goshenite (no coloring impurity).
Hereinafter, in referring to the starting material, the
term "beryl" will include a proper proportioned mixture
of the constituents of beryl and all the members of the
beryl family.

In particular the method comprises melting beryl and
subsequently allowing it to solidify with the melting and
solidification steps being carried out under pressure. It
has been found that if clear transparent crystals of beryl
are heated to temperatures above 600° C., there is a
molecular dissociation and self-diffusion of some of the
constituents of beryl through the crystal, said diffusion
destroying its optical properties. Consequently, if an at-
tempt is made to form beryl crystals by melting beryl,
self-diffusion of the constituents of beryl would prevent
the formation of clear, transparent crystals. It has been
found that this problem can be obviated by the applica-
tion of pressure during the melting and cooling steps.

The pressure is only critical in that it must be high
enough to prevent self-diffusion, yet not so high that it
prevents the beryl from expanding during solidification.
Beryl has a negative coefficient of expansion in a direction
parallel to the hexagonal crystal axis and thus during
solidification it will expand in one direction and contract
in the other. If the pressure is so high that this expansion
can not occur, no crystals will be formed. Although beryl
crystals can be formed at any pressure that is sufficient
to both prevent self-diffusion of the beryl constituents
through the crystal and allow expansion of the crystal
during solidification, as a practical matter the minimum
and maximum pressures that are used are dictated by the
particular pressure system employed. For example, in
the apparatus depicted in FIGS. 1 and 2 which is de-
scribed more fully below, it has been found that due to
the closed capsule employed the pressure should not ex-
ceed about 20 kilobars and preferably should not exceed
about 15 kilobars. It has been found that good results
are obtained in this apparatus if the pressure is main-
tained between about 7.5 and 15 kilobars.

The temperature employed is any temperature which
is sufficient to melt the beryl without decomposing it
(when the constituents of beryl are employed they melt
and combine to form beryl) and of course this melting
temperature is a function of pressure, with the change
being about 40° C. per kilobar (beryl melts at 1410° C.
at atm. pressure and 1800° C. at 10 kilobars). Once the
beryl is uniformly melted, temperature reduction may
be started almost instantaneously and this reduction in
temperature may be effected abruptly or over a period
of time without any significant change in results.

It is also possible to solidfy the beryl after melting by
raising the pressure rather than diminishing the tempera-
ture. For example, the beryl can be melted at 1800° C.
at a pressure of 10 kilobars and then be solidified by
raising the pressure, e.g. to about 20 kilobars while main-
taining the same temperature or any temperature that is
below the melting point of beryl at 20 kilobars.

The high temperatures used in the method of this inven-
tion introduces limitations as to the material employed
as the capsule for the beryl. If the capsule material melts
at the temperatures employed, it will diffuse through the
beryl preventing the formation of a single clear crystal
and therefore the capsule must be made from a material
that does not react with or diffuse into the beryl, i.e. it
must be inert at high temperatures. It has been found that
carbon in the form of graphite is an excellent capsule
material at all pressures (melted beryl has been held in
such a capsule for as long as one-half hour at 15 kilobars
without reaction, mixing or diffusion processes occurring)

with carbon lined materials such as carbon lined Vycor glass giving equally good results. Capsules formed from platinum and tungsten are not as effective since the melting and solidification must be performed rapidly in order to prevent diffusion. Another means of avoiding the reaction and diffusion problem is to employ one of the constituents of beryl itself, e.g. BeO as the capsule material.

The process of this invention may be carried out in apparatus such as is shown generally as 10 in FIG. 1. This apparatus is of the so-called stepped-core type and is composed of a plurality of concentric binding rings 11–15 inclusive, surrounding a tungsten carbide core 16. Core 16 has a cylindrical bore 17 therethrough, and counterbores 18 and 19 opening into each end thereof. In coaxial alignment with bore 17 are two press pistons 23 and 24 having tungsten carbide end elements 26 and 27 configured to cooperate with counterbores 18 and 19 and bore 17 in order to impose pressure on the sample contained within bore 17. Pistons 23 and 24 are biased toward one another by apparatus (not shown) which may be a hydraulic press as is well known in the art. The particular apparatus used by the inventors is a 300 ton press.

The same container 28 is shown in detail in FIG. 2. The material to be crystallized in the process is diagrammatically shown at 29 as contained within a closed capsule 31. Capsule 31 is disposed within a pressed talc cylinder 32 which is in turn supported within a carbon cylinder 33 which serves as a heat source when electric current is passed therethrough. Disposed within the talc cylinder 32 at each end of the sample capsule 31 are pyrophyllite plugs 34 and 35 and surrounding the outside of the carbon cylinder 33 is a body of pyrophyllite 36 which is configured to fit within bore 17. Completing the container assembly are a pair of electrically conductive end caps 37 and 38 which are disposed in counterbores in pyrophyllite cylinder 36 and are in electrical contact with the carbon cylinder 33. Electrical contact is made to the outside of end caps 37 and 38 through the press pistons themselves, current being supplied to the press pistons by conductors 39 and 40. Counterbores 18 and 19 are also provided with annular pyrophyllite members 43 and 44, which along with the pyrophyllite in the sample container and the pressed talc cylinder serves to transmit pressure to the sample. With this apparatus it is possible to obtain pressures up to 60,000 atmospheres in the capsule.

The process is carried out in the apparatus by first adjusting the pressure to the proper value. The temperature is then raised until the powder melts by passing an electric current through carbon cylinder 33. The electric current is then abruptly cut off. Since there is a large mass of steel surrounding the sample the temperature is reduced to nearly room temperature in a matter of a few minutes. Under these conditions, the melt fuses into a single crystal of beryl which is removed from the press after the pressure has been reduced.

It is to be understood, however, that the method of this invention is not to be limited to the apparatus described above since the process may be performed by any means which can effect melting and solidification under pressure. It should also be apparent that many modifications can be made in the apparatus described above without departing from its general concept, e.g. some or all of the pyrophyllite members may be replaced by another pressure transmitting material such as boron nitride.

The process of this invention may be employed to form any of the crystalline members of the beryl family (aquamarine, goshenite, emerald, golden beryl and morganite) by adding the ionic impurity that gives the particular member its characteristic color. For example, if it is desired to produce emerald crystals, chromium ions are added to the beryl sample before melting and cooling under pressure, the chromium ions giving the finished crystal the characteristic green color of emeralds. The chromium ions may be introduced by adding an amount of $Cr_2O_3$ to the beryl that does not exceed about 2 weight percent, preferably between about 0.5 and 1 weight per-

cent with 1 weight percent giving especially good results. Although the process described above is wholly satisfactory for the creation of large clear single crystals, many modifications can be made without departing from the spirit of the invention. For example, water can be added to the beryl sample to reduce the temperature coefficient, said reduction effecting a lowering of the process temperatures (1 weight percent of water reduces the melting point of beryl from about 2000° C. to about 1500° C. at 15 kilobars).

Although water addition has a beneficial effect on process conditions, an excess of water adversely effects crystallization and from theoretical calculations it has been determined that the total amount of water present should not exceed about 6.5 weight percent. Since beryl may already contain some water (for example, beryl samples used in the form of goshenite usually contain enough water to effect such a reduction without water addition), the water content should not exceed about 2 weight percent preferably not in excess of 1 weight percent.

It has been found that the temperature of melting can be reduced even further by using fluorine gas as a flux. One way to obtain the fluorine is to use "Teflon" as a capsule material. At a temperature near 800° C., the "Teflon" dissociates to give off fluorine which causes the beryl to melt in the neighborhood of 1000° C. at 20 kilobars pressure. Another way to obtain the fluorine is to use $CrF_3$ in place of $Cr_2O_3$ as the coloring agent. When this is done, the fluorine gas is given off at 1000° C. at 15 kilobars.

In another alternative embodiment, the pressure is established at 10 kilobars and the temperature is raised to 1000° C., a temperature well below the melting temperature of the beryl and container material. The conditions of temperature and pressure must be held for a much longer time under these conditions in order to obtain sizeable crystals. In one example, the conditions were held for a period of 25 minutes, resulting in small microscopic crystals of beryl, while the major portion of the sample had the appearance of a granular rock. Much longer times are required to achieve larger crystals.

In a further embodiment, the beryl sample is melted at one pressure, e.g. 15 kilobars and then immediately dropped to a lower pressure, e.g. 7.5 kilobars for the cooling and solidification. It has been found that such a procedure may prevent the laminate formation that may occur if cooling is effected at higher pressures.

The following examples illustrate a specific embodiment of the invention but its scope is not to be limited thereby.

### Example I

Beryl powder (aquamarine) mixed with 2% $Cr_2O_3$ and 1% $H_2O$ was placed in a tungsten capsule and subjected to a pressure of 15 kilobars and a temperature of 1570° C. for two minutes in the apparatus of FIG. 1. After cooling and reducing the pressure, a single clear crystal was removed from the capsule which proved to be emerald.

### Example II

Similarly to Example I, beryl powder (aquamarine) mixed with 2% $Cr_2O_3$ and 1% $H_2O$ was placed in a tungsten capsule and subjected to a pressure of 15 kilobars and a temperature of 1470° C. for two minutes. After cooling, emerald crystal having a density of 2,716 was removed from the capsule.

### Example III

Similarly to Example I, beryl powder (aquamarine) mixed with 1% $Cr_2O_3$ and 1% $H_2O$ was placed in a carbon capsule and subjected to a pressure of 15 kilobars and a temperature of 1425° C. for five minutes. After cooling, it was found that single emerald crystal formed throughout the capsule.

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### Example IV

Similarly to Example I, beryl powder (goshenite) mixed with 0.5% $Cr_2O_3$ was placed in a carbon lined Vycor glass capsule and subjected to a pressure of 15 kilobars and a temperature of 1535° C. After cooling it was found that single emerald crystal formed throughout the capsule.

### Example V

A mixture was prepared by combining 6.98 g. BeO, 9.485 g. $Al_2O_3$ and 35.53 $SiO_2$. To this mixture there was added 2 weight percent $Cr_2O_3$ and 2 weight percent $H_2O$ and the mixture was placed in a tantalum capsule.

The mixture was subjected to a temperature of 2015° C. and a pressure of 15 kilobars for two minutes. The temperature was dropped rapidly and a single emerald crystal was formed in the capsule.

### Example VI

The mixture employed in Example V was heated at 2000° C. and 15 kilobars for one minute in a tantalum capsule. After rapid cooling it was found that emerald crystal formed throughout the capsule.

The method of this invention may be easily performed in any pressure system which is sufficient to produce a pressure that will prevent diffusion of the beryl constituents during melting and solidification. The opticum conditions employed will vary from system to system and they may be easily determined by those skilled in the art from the teaching of this disclosure that the starting material may be melted and solidified under any pressure that prevents diffusion of the constituents and allows expansion of the crystal.

The method of this invention is extremely effective for producing single clear beryl crystals. The starting materials, beryl in any of its forms or the constituents of beryl, are readily available and any member of the beryl family can be produced by adding the proper coloring agent. Unlike previous processes for forming beryl crystals, the process of this invention is extremely rapid since the crystal can be formed as quickly as the starting material can be melted and solidified under pressure.

The method of this invention is especially valuable for the production of emerald crystals, since this particular form of beryl, as well as being a valuable gem, has particular utility in laser and maser technology. The emeralds produced by this invention have hardness, density, and optical properties that are far superior to any synthetic emeralds that have been produced in the past.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood, that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method for producing beryl crystals which comprises melting a member selected from the group consisting of beryl powder and a mixture of the constituents of beryl in their proper proportions, and solidifying said member to produce beryl crystal, said melting and solidification being performed at a pressure sufficiently high to prevent self-diffusion of the constituents of beryl through the crystals yet not so high as to prevent expansion thereof during solidification.

2. The method of claim 1 wherein said member is beryl powder.

3. The method of claim 1 wherein said member is beryl powder in the form of goshenite.

4. The method of claim 1 wherein said member is beryl powder in the form of aquamarine.

5. The method of claim 1 wherein said member is the constituents of beryl in their proper proportions.

6. The method of claim 1 wherein said member contains an amount of water that does not exceed about 2 weight percent.

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7. A method for producing emerald crystals which comprises, melting a member selected from the group consisting of beryl powder and a mixture of the constituents of beryl in their proper proportions, said member containing chromium ions, and solidifying said member to form emerald crystals, said melting and solidification being performed at a pressure sufficiently high to prevent self-diffusion of the constituents of beryl through the crystal yet not so high as to prevent expansion thereof during solidification.

8. The method of claim 7 wherein said member is beryl powder.

9. The method of claim 7 wherein said member is beryl powder in the form of goshenite.

10. The method of claim 7 wherein said member is a mixture of the constituents of beryl in their proper proportions.

11. The method of claim 7 wherein said member contains an amount of water that does not exceed about 6 weight percent.

12. A method for producing emerald crystals which comprises melting a mixture of beryl powder and $Cr_2O_3$, said $Cr_2O_3$ being present in an amount not exceeding about 2 weight percent and solidifying said mixture to form emerald crystal, said melting and solidification being performed at a pressure sufficiently high to prevent self-diffusion of the constituents of beryl through the crystal yet not so high as to prevent expansion thereof during solidification.

13. The method of claim 12 wherein the beryl powder is in the form of goshenite.

14. The method of claim 12 wherein the beryl powder is in the form of aquamarine.

15. The method of claim 12 wherein the mixture contains an amount of water that does not exceed about 2 weight percent.

16. A method for producing emerald crystals which comprises melting a mixture of the constituents of beryl in their proper proportions, said mixture also containing $Cr_2O_3$ in an amount that does not exceed about 2 weight percent, and solidifying the mixture to produce emerald crystal, said melting and solidification being effected at a pressure sufficiently high to prevent self-diffusion of the constituents of beryl through the crystal yet not so high as to prevent expansion thereof during solidification.

17. The method of claim 16 wherein the mixture contains an amount of water that does not exceed about 2 weight percent.

18. A method for producing emerald crystals which comprises melting a mixture of $Cr_2O_3$ and a member selected from the group consisting of beryl powder and a mixture of the constituents of beryl in their proper proportions, said $Cr_2O_3$ being present in an amount that does not exceed about 2 weight percent, and solidifying the mixture to form emerald crystal, said melting and solidification being performed at a pressure that ranges from about 7.5 to 15 kilobars.

19. The method of claim 18 wherein the mixture contains an amount of water that does not exceed about 2 weight percent.

20. A method for producing emerald crystals which comprises,

(a) placing a mixture of $Cr_2O_3$ and a member selected from the group consisting of beryl powder and a mixture of the constituents of beryl in their proper proportions in a capsule, formed from material inert at high temperatures said $Cr_2O_3$ being present in an amount not exceeding about 2 weight percent,

(b) placing said capsule in a pressure vessel having an electric heating element therein,

(c) raising the pressure on said capsule to a pressure between 7.5 and 15 kilobars,

(d) passing an electric current through said heating element to heat the mixture to its melting point under the established pressure, and

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(e) solidifying the melt to produce emerald crystal.

21. The method of claim 20 wherein the capsule is formed from a member selected from the group consisting of carbon and carbon lined materials.

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HELEN McCARTHY, Primary Examiner

U.S. Cl. X.R.

23—110

*Fig. 1.*

*Fig. 3.*

*Fig. 2.*

*Fig. 4.*
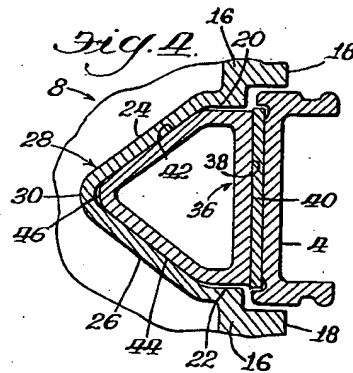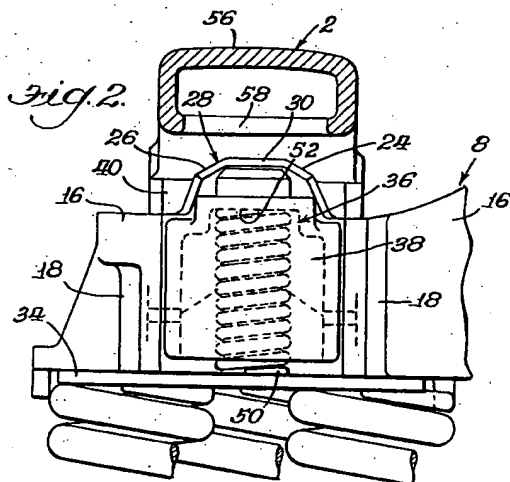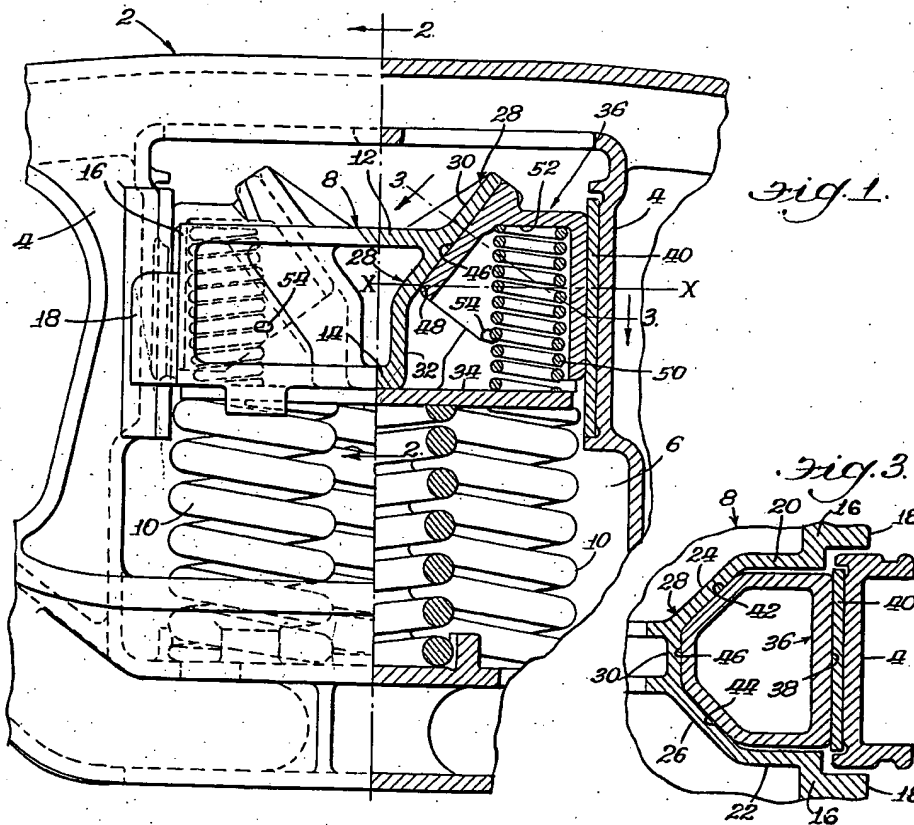
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By Walter L. Schlegel, Jr.
Atty.

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This invention relates to railway car trucks and more
particularly to a truck in which novel means are pro-
vided for snubbing oscillations of the bolster relative to
its supporting side frames and for returning the bolster
to normal perpendicular relationship with respect to said
frames after the bolster has been forced to an out-of-
square relationship with respect to the side frames, as for
example, when the truck proceeds around a curved sec-
tion of track.

A primary object of the invention is to afford maxi-
mum bearing area between the bolster and friction shoes
in an arrangement wherein the shoes are urged against
the bolster and side frame columns by springs maintained
under pressure against portions of the bolster structure.

Another object of the invention is to afford in a truck
such as above described, shoe actuating springs of maxi-
mum length and capacity.

Yet another object of the invention is to improve the
manner in which the friction shoes urge the bolster to
perpendicular relationship with respect to the support-
ing side frames.

The foregoing and other objects and advantages of
the invention will become apparent from a considera-
tion of the following specification and the accompany-
ing drawings wherein:

Figure 1 is a fragmentary side elevational view, partly
in central vertical section, illustrating an embodiment
of the invention;

Figure 2 is a sectional view of the side frame taken on
line 2—2 of Figure 1, with the bolster and its support-
ing springs illustrated in elevation;

Figure 3 is a sectional view on line 3—3 of Figure 1,
and

Figure 4 is a sectional view corresponding to Figure 3
but illustrating a modification of the invention.

Describing the invention in detail and referring to the
drawings, it will be understood that the truck comprises
a pair of side frames, one of which is illustrated at 2.
The side frame comprises spaced columns 4 partly defin-
ing a bolster opening 6 within which one end of a bolster
8 is supported as by springs 10 carried by the frame 2.

The bolster 8 comprises top and bottom walls 12 and
14, respectively, and spaced side walls 16 having gibs 18
loosely interlocking each end of the bolster with related
side frame columns 4 to permit oscillation of the bolster
vertically as well as longitudinally and laterally with
respect to side frames and to afford movement of the
bolster to an out-of-square relationship with respect to
the side frame 2, as heretofore described. As best seen
in Figure 3, each side wall 16 is connected by inboard
and outboard substantially parallel webs 20 and 22, re-
spectively to segments 24 and 26 of a bolster web gen-
erally designated 28, said web comprising another seg-
ment 30 extending between and connected to the seg-
ments 24 and 26. The bottom of web 28 is connected
to a substantially vertical bolster web 32 which merges
with the bottom wall 14.

The bolster, as illustrated, is a multi-part structure in-

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cluding a spring plate 34, at each end thereof mounted
on the springs 10 and supporting the bottom wall 14.
However, if desired, as is well known in the art, the
bolster 8 may be a one-piece cast structure with the
spring plate 34 integral with the bottom wall 14.

Associated with each web 28 is a friction shoe gener-
ally designated 36, said shoe having a friction face 38
frictionally engaged with a wear plate 40 which may be
mounted in any desired manner, as by welding, on the
related side frame column 4 or may be integral therewith
as desired. The shoe comprises wedge surfaces 42 and
44 which engage segments 24 and 26 of the bolster web
28, and the shoe also comprises a wedge surface 46
which engages segment 30 of the web 28.

As best seen in Figure 1, the web 28, including all
three segments 24, 26 and 30 thereof, slopes downwardly
at an acute angle with respect to the longitudinal vertical
center plane of the bolster indicated by the line 2—2
of Figure 1. Moreover, as best seen in Figure 3, the
segments 24 and 26 converge with respect to each other
toward said plane and at an acute angle. The sides of
shoe 36 are spaced from the bolster webs 20 and 22 as
seen in Figure 3 to accommodate movement of the bol-
ster lengthwise thereof, with respect to the side frame
and to accommodate movement of the bolster to out-of-
square relationship with respect to the side frame as here-
tofore described. The gibs 18 are similarly spaced and
for the same purpose form the inboard and outboard
wedges of column 4.

It may be noted, that the engagement of shoe surface
46 with the segment 30 of the bolster web 28 preferably
represents a worn-in condition which occurs after shoe
surfaces 42 and 44, as well as the engaged surfaces of
segments 24 and 26 have worn in service. Thus, it will
be understood that the shoe surface 46 may if desired,
be initially spaced from the segment 30 and arranged to
engage the latter after such wearing in of the other re-
lated surfaces, as heretofore described.

The lowermost point of wedge engagement between
bolster web 28 and the friction shoe 36 is preferably
spaced (along a horizontal plane) from the vertical cen-
ter plane of the bolster, a distance substantially less than
one-quarter of the distance between said center plane
and the wear plate 40 along said horizontal plane. This
relationship is significant in combination with the con-
struction and arrangement of wedge surfaces 42, 44 and
46, in affording maximum bearing of the shoe against the
bolster in such an arrangement. Thus, the lowermost
point of engagement between the shoe 36 and the bolster
web 28 is depicted in Figure 1 at 48 and is spaced along
a horizontal plane X—X from the vertical center plane
of the bolster indicated by line 2—2, a distance which is
clearly less than twenty five percent of the distance along
said horizontal plane from center line 2—2 to the wear
plate 40. This novel arrangement affords a condition in
which the combined bearing area of the shoe against the
bolster web 28 along segment 24, 26 and 30 thereof is
greater than two-thirds of the area of the shoe face 38,
hereby affording an arrangement capable of long life in
service and unusual bolster stability during movements
thereof, as heretofore described.

Each friction shoe is actuated by a spring 50 com-
pressed against the spring plate 34 and against a spring
seat 52 of friction shoe which is preferably disposed
above the level of the top of the bolster wall 12 and in
any event is disposed above the level of the bottom of
the bolster wall 12 to afford a spring 50 of maximum
length and capacity for the development of frictional
and resilient resistance to various bolster movements
relative to the side frame 2.

The bolster webs 20 and 22 and each friction shoe
may be provided with openings indicated at 54 in Figure

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1 for the purpose of receiving a key to lock the shoe and spring in inoperative position during assembly and disassembly of the truck.

Also, as best seen in Figure 2, the top or compression member 56 of the side frame 2 is provided with an open- 5 ing 58 above each friction shoe for the reception of the upper end of shoe and the bolster web 28 as the bolster is elevated to the top bolster opening 6 during assembly and disassembly of the springs 10.

Figure 4 is a sectional view corresponding to Figure 10 3, but illustrating a modification of the invention wherein parts corresponding to those previously described in connection with Figures 1–3 are identified by corresponding numerals. In the modification of Figure 4, segments 24 and 26 of the bolster web 28 are somewhat 15 longer than in the embodiment shown in Figure 3 and the segment 30 is arcuate, so that the segments 24, 26 and 30 define a generally V-shaped web 28 which is otherwise substantially identical with the corresponding web of the embodiment shown in Figures 1–3. 20

It may be noted that in the modification of Figure 4, shoe surface 46 is illustrated as spaced from the bolster web segment 30, as would be the case in a new construction. However, it will be understood by those skilled in the art, that as the wedge surfaces 42 and 44 25 of the shoe and the engaged surfaces of segments 24 and 26 wear in service, the shoe surface 46 gradually moves into abutment with the segment 30 of web 28. The combined area of shoe surfaces 42 and 44 in the modification is 23¼ square inches, and the friction face 38 30 has an area of 27½ square inches, as compared with values of 14¼ square inches of wedge face area and 27⅝ square inches of friction face area in prior art trucks of this type.

We claim: 35

1. A railway car truck comprising a side frame having a column with a friction surface, a bolster structure spring-supported by said frame, and comprising top and bottom walls and spaced side walls, a web at each side of the bolster structure connected to the top wall and to 40 a related side wall, said web sloping at an acute angle with respect to the vertical and comprising inboard and outboard segments converging with respect to each other at an acute angle toward the longitudinal vertical center plane of the bolster structure, said structure having 45 another web connecting the bottom of said first-mentioned web to the bottom wall, friction shoe means having a substantially horizontal spring seat above the level of the bottom of said top wall, said shoe means having friction means engaged with said friction sur- 50 face, said shoe means being in complementary wedge face engagement with said sloping web at least along said segments thereof, the lowermost point of said wedge face engagement being spaced, along a horizontal plane, a distance from said center plane less than 25% of the 55 distance between said center plane and said friction surface along said horizontal plane, the total area of said wedge face engagement between the shoe means and the sloping web being greater than two-thirds of the area of said friction means, and spring means compressed 60 on a substantially vertical axis between said bottom wall and said seat for actuation of said shoe means.

2. A railway car truck according to claim 1, wherein the wedge face engagement of the shoe means and sloping web extends a substantial distance above the upper 65 level of the friction means.

3. A railway car truck according to claim 1, wherein the wedge face engagement of the shoe means and the sloping web extends along a substantially flat area of the sloping web between said segments. 70

4. A railway car truck comprising a side frame having a column with a friction surface, a bolster structure spring-supported by said frame and comprising top and bottom walls and spaced side walls, a web at each side of the bolster structure connected to the top wall, 75

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said web sloping at an acute angle with respect to the vertical and comprising inboard and outboard segments converging with respect to each other at an acute angle and toward the longitudinal vertical center plane of the bolster structure, friction shoe means having a substantially horizontal spring seat above the level of the bottom of said top wall, said shoe means having friction means engaged with said friction surface, said shoe means being in complementary wedge face engagement with said web at least along said segments thereof, the total area of engagement between the shoe means and web being substantially greater than two-thirds of the area of said friction means, and spring means compressed between said bottom wall and said seat for actuation of said shoe means.

5. A railway car truck according to claim 4, wherein the wedge face engagement of the shoe means and bolster web extends a substantial distance above the upper level of the friction means.

6. A railway car truck according to claim 4, wherein the wedge face engagement of the shoe means and the sloping web extends along a substantially flat area of the sloping web between said segments.

7. A railway car truck having a side frame with spaced columns defining therebetween a bolster opening, spring means disposed in said bolster opening and being supported by said frame, a spring plate on said spring means, a bolster disposed in said opening and engaging said plate, said bolster having spaced top and bottom walls, a web connecting said walls and having a plurality of segments converging and mateably joining with each other forming a pocket therebetween, said segments being inclined acutely with the vertical and extending upwardly and outwardly from the longitudinal center plane of said bolster and being above and below said top wall, friction shoe means disposed in said pocket and being in complementary engagement with said segments, said shoe means having a friction surface for sliding engagement with said column, other spring means disposed between and abutting said shoe means and said spring plate for urging said shoe means into said engagements.

8. A railway car truck according to claim 7 wherein said pocket is defined by a five sided cross section open at only one end, two of said sides being oppositely facing, the third of said sides being disposed substantially perpendicularly to said two sides, and the fourth and fifth sides being angularly disposed between and mergingly connecting said two sides with said third side, respectively.

9. A railway truck comprising a side frame having spaced columns with friction surfaces thereon, a bolster resiliently supported on said frame and being disposed between said columns, said bolster having a longitudinal vertical center plane disposed substantially centrally of said friction surfaces, said bolster having spaced top and bottom walls interconnected by webs, each of said webs having a vertical portion and an inclined portion mergingly joining each other along a line, said line being disposed so as to be less than 25% of the horizontal distance from said plane to one of said friction surfaces, said inclined portion extending upwardly and outwardly from said vertical portion and comprising segments angularly disposed with each other and defining therebetween pockets, friction shoes having wedge surfaces angularly disposed with each other and being mateably received within said pockets and being slidably engageable with said segments, said shoes having friction faces slidably engageable with said friction surfaces, and spring means disposed between and abutting said shoes and said bolster for urging said shoes into said engagements.

10. In a railway car truck, a side frame having a friction surface, a bolster resiliently supported on said frame and being adjacent said surface, said bolster having top and bottom walls interconnected by webs, said webs

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comprising a plurality of segments angularly disposed with each other and being inclined acutely with the vertical, said segments extending above and below said top wall, a friction shoe having a friction face engageable with said surface, said shoe having wedge surfaces angularly disposed with each other and being inclined acutely with the vertical, said wedge surfaces and said segments being slidably engageable, spring means abutting said shoe and said bolster for urging said shoe into said engagements, the abutment with said shoe being disposed above the top wall of said bolster.

11. A railway car truck according to claim 10, wherein the total area of the engagement of said shoe with said bolster is greater than two thirds of the total area of the engagement of said shoe with said friction surface.

12. A railway car truck having a side frame with spaced friction surfaces, a bolster resiliently supported on said frame and having spaced top and bottom walls, webs interconnecting said walls, said webs having vertical portions thereof spaced from the longitudinal vertical center plane of said bolster and inclined portions thereof extending upwardly acutely from the vertical and outwardly from said center plane, said vertical por-

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tion being connected to and abuttingly joining said bottom wall and said inclined portions being connected to and extending above and below said top wall, respectively, said portions defining outwardly facing pockets, friction shoe means disposed in the respective pockets and having wedge surfaces inclined acutely with the vertical and being mateably engageable with the inclined portions of said webs, said shoe means having friction faces engageable with said friction surfaces, respectively, and spring means disposed between the shoe means and the bolster and urging said shoe means against the friction surfaces of the frame and the inclined portions of the bolster, respectively.

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